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Molecular Weight of Electropolymerized Polyaniline

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Polyaniline was electropolymerized on a platinum electrode and the molecular weight determined by gel permeation chromatography.

Electropolymerized polymers have received considerable attention recently[1—11] owing to their good electrical conductivity and wide application in electrochemistry. However, there are few reports on the molecular weight and distribution of the electrodeposited product, and about the effect of electrochemical conditions, such as potential, current density, *etc.* The difficulty in characterization is attributable to the insolubility of the electropolymerized conductive polymer. The conductivity is based on a charge-transfer complex in the polymer backbone[3,4] and complexation decreases the solubility. Polyaniline is doped with anions such as SO_4^{2-}, Cl^-, ClO_4^- *etc.* We now report a technique for solubilization of polyaniline and determination of its molecular weight by gel permeation chromatography (g.p.c.).

Polyaniline was produced on a platinum electrode in 0.1 M aniline–0.1 M H_2SO_4 solution either by a potentiostatic or a potential sweep method. Polyaniline films show a blue colour and are insoluble in any solvent, *e.g.* tetrahydrofuran (THF). We used 20 wt% aqueous NaOH–THF (1 : 3 v/v) to extract the products. The mixture was separated into two phases, and the THF phase gradually showed the blue colour of polyaniline with increased extraction time. Excessive extraction time, however, decreased the blue colour, suggesting that 'undoping' of SO_4^{2-} anion took place, which must be performed by NaOH. It is known that electropolymerized conductive polymers change colour according to the doping state.[12]

The g.p.c. elution patterns of polyaniline extracted with THF solvent are shown in Figure 1. The polyaniline was electropolymerized by a potentiostatic method. The anodic peak potential, based on the oxidation of aniline, appeared at about 0.9 V *vs.* standard calomel electrode (s.c.e.) on cyclic voltammetry. Electropolymerization was performed at this peak potential for 12 h. The abscissa in Figure 1 is converted to molecular weight from elution time, the molecular weight being determined using monodispersed polystyrene as a standard. The ordinate in Figure 1 is weight fraction (arbitrary). Figure 1(a) shows the elution pattern of polyaniline extracted for 1 h and Figure 1(b) shows that extracted for 24 h. The elution peak appeared around M = 9000 in Figure 1(a). The extraction method is not quantitative for the determination of the molecular weight fraction because a small amount of insoluble residue (which may be a higher molecular weight fraction) remains in the extracting solution. However, Figure 1(a) suggests, at least, that the electrodeposited product, 'poly'aniline, is not an oligomer but a polymer with a fraction whose molecular weight is higher than 9000.

The molecular weight decreased with increasing extraction time. After 24 h [Figure 1(b)], three sharp peaks had appeared and the peak of higher molecular weight in Figure 1(a) had

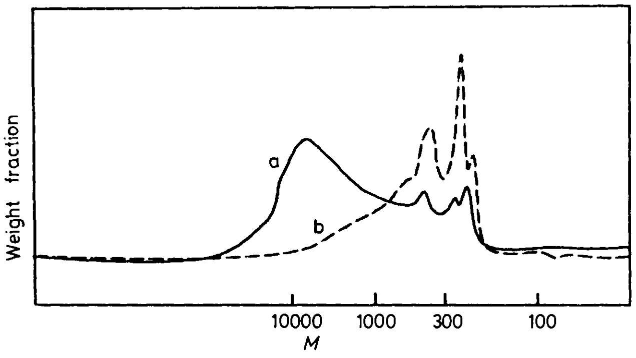

Figure 1. The g.p.c. elution patterns of polyaniline electropolymerized by a potentiostatic method. *Conditions:* 0.9 V *vs.* s.c.e., 12 h. (a) extracted for 1 h, (b) extracted for 24 h.

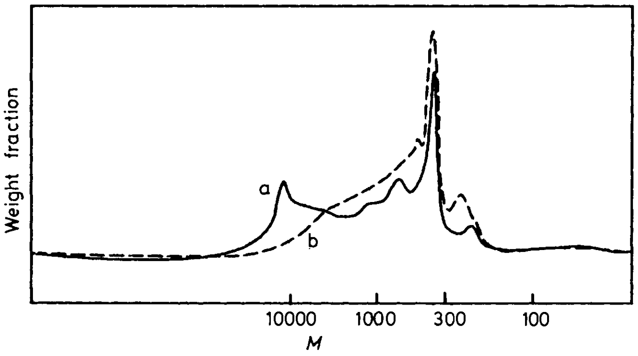

Figure 2. The g.p.c. elution patterns of polyaniline electropolymerized by a potential sweep method. *Conditions:* sweep range −0.7—1.3 V *vs.* s.c.e., sweep rate 16.7 mV/s, 10 h; (a) extracted for 1 h, (b) extracted for 24 h.

disappeared. This suggests that the decomposition of polyaniline takes place in the process of extraction by the aq. NaOH–THF solution and undoping of SO_4^{2-}.

The g.p.c. elution patterns of polyaniline electropolymerized by a potential sweep method (sweep range −0.7—1.3 V *vs.* s.c.e., sweep rate 16.7 mV/s, 10 h) are shown in Figure 2. The elution pattern [Figure 2(a)] shows a broad distribution of molecular weight compared to Figure 1(a) (potentiostatic method). The broad distribution must be caused by various electrochemical reactions during the potential sweep between −0.7 and 1.3 V *vs.* s.c.e.

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